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(54) Title: GRANULES BASED ON PYROGENICALLY PREPARED SILICON DIOXIDE, A PROCESS FOR THEIR PREPARATION AND THEIR USE

(57) Abstract: Granules based on pyrogenically prepared silicon dioxide with the following physico-chemical characteristic data: Average particle diameter: 10 to 120 µm BET surface area: 40 to 400 m<sup>2</sup>/g Pore volume: 0.5 to 2.5 ml/g Pore distribution: content of pores of pore diameter < 5 nm in the total pore volume of less than 5%, remainder meso- and macropores Tamped density: 220 to 1,000 g/l Numerical content of particles in the particle size range above the D10 value of the particle size distribution weighted according to volume which have tucks or closed off inner hollow spaces: < 35 % They are prepared by a procedure in which silicon dioxide is dispersed in a liquid, preferably water, together with one or more auxiliaries, the dispersion is spray dried and the granules are optionally heat-treated and/or silanized. The granules are employed as a catalyst support.

**Granules based on pyrogenically prepared silicon dioxide, a process for their preparation and their use**

The invention relates to granules based on pyrogenically prepared silicon dioxide, the process for their preparation 5 and their use as a catalyst support.

It is known to prepare pyrogenic silicas or silicon dioxides from  $\text{SiCl}_4$  by means of high temperature or flame hydrolysis (Ullmanns Enzyklopädie der technischen Chemie [Ullmanns Encyclopaedia of Industrial Chemistry], 4th 10 edition, volume 21, page 464 (1982)).

Pyrogenic silicon dioxides are distinguished by an extreme fine division, a high specific surface area (BET), a very high purity, a spherical particle shape and the absence of pores. On the basis of these properties, pyrogenically 15 prepared silicon dioxides are finding increasing interest as supports for catalysts (Dr. Koth et al., Chem. Ing. Techn. 52, 628 (1980)). For this use, the pyrogenically prepared silicon dioxide is shaped by a mechanical route by means of, for example, tablet-making machines.

20 It is also known to shape pyrogenically prepared silicon dioxide to spray granules by means of spray drying. US 5776240 describes granules based on pyrogenic silicon dioxide which are obtainable by spray drying an aqueous suspension of pyrogenic silicon dioxide. Granules which are 25 prepared in such a manner have the disadvantage that they have tucks on the surface (amphore formation), inner hollow spaces and deformations. Such effects are well-known in spray drying (K. Masters, Spray Drying, 2<sup>nd</sup> ed., 1976, John Wiley & Sons, New York, p. 329). These morphological 30 defects have an adverse effect in the use as a catalyst support. In olefin polymerization, for example, the form of the catalyst support is copied by the polymer grain due to the replica effect. This likewise results in hollow spaces and deformations in the polymer, which lower the bulk

density (and therefore the capacity of the polymerization plant) or can have the effect of inclusion of monomers, which has an adverse effect in further processing. When used as a support for other fluidized bed catalysts, these 5 defects lead to increased abrasion and therefore increased catalyst consumption.

There was therefore the object of developing improved spray granules of pyrogenically prepared silicon dioxide which can be employed as a catalyst support for olefin 10 polymerization or other catalytic fluidized bed processes. These should be distinguished by a lower content of particles with tucks and hollow spaces compared with the prior art.

The invention provides granules based on pyrogenically 15 prepared silicon dioxide with the following physico-chemical characteristic data:

Average particle diameter:	10 to 120 $\mu\text{m}$
BET surface area:	40 to 400 $\text{m}^2/\text{g}$
Pore volume:	0.5 to 2.5 ml/g
20 Pore distribution:	content of pores of pore diameter < 5 nm in the total pore volume of less than 5%, remainder meso- and macropores
Tamped density:	220 to 1,000 g/l
Numerical content of particles in the particle size range 25 above the D10 value of the particle size distribution weighted according to volume which have tucks or closed off inner hollow spaces:	< 35 %

The granules according to the invention can be prepared by a procedure in which silicon dioxide prepared from a 30 volatile silicon compound by means of flame hydrolysis is dispersed in a liquid, preferably water, with one or more organic or inorganic auxiliary substances, the dispersion is spray dried and the granules obtained are optionally

heat-treated at a temperature of 150 to 1,100°C and/or silanized.

Halogenosilanes, alkoxy silanes, silazanes and/or siloxanes can be employed for the silanization.

5 The following substances can be employed in particular as halogenosilanes:

Halogeno-organosilanes of the type  $X_3Si(C_nH_{2n+1})$       X = Cl, Br  
    n = 1 - 20

10 Halogeno-organosilanes of the type  $X_2(R')Si(C_nH_{2n+1})$  X = Cl, Br  
    R' = alkyl  
    n = 1 - 20

Halogeno-organosilanes of the type  $X(R')_2Si(C_nH_{2n+1})$  X = Cl, Br  
    R' = alkyl  
    n = 1 - 20

15 Halogeno-organosilanes of the type  $X_3Si(CH_2)_mR'$

X = Cl, Br

m = 0,1 - 20

R' = alkyl, aryl (e.g.  $-C_6H_5$ )

- $C_4F_9$ , - $OCF_2-CHF-CF_3$ , - $C_6F_{13}$ , - $O-CF_2-CHF_2$

20 - $NH_2$ , - $N_3$ , - $SCN$ , - $CH=CH_2$ ,

- $OOC(CH_3)C=CH_2$

- $OCH_2-CH(O)CH_2$

- $NH-CO-N-CO-(CH_2)_5$

- $NH-COO-CH_3$ , - $NH-COO-CH_2-CH_3$ , - $NH-(CH_2)_3Si(OR)_3$

25 - $S_x-(CH_2)_3Si(OR)_3$

Halogeno-organosilanes of the type  $(R)X_2Si(CH_2)_mR'$

X = Cl, Br

R = alkyl

30 m = 0,1 - 20

R' = alkyl, aryl (e.g.  $-C_6H_5$ )

- $C_4F_9$ , - $OCF_2-CHF-CF_3$ , - $C_6F_{13}$ , - $O-CF_2-CHF_2$

- $NH_2$ , - $N_3$ , - $SCN$ , - $CH=CH_2$ ,

- $OOC(CH_3)C=CH_2$



$-\text{NH}-\text{COO}-\text{CH}_3$ ,  $-\text{NH}-\text{COO}-\text{CH}_2-\text{CH}_3$ ,  $-\text{NH}- (\text{CH}_2)_3\text{Si}(\text{OR})_3$   
 $-\text{S}_x-(\text{CH}_2)_3\text{Si}(\text{OR})_3$

Organosilanes of the type  $(\text{R}'')_x(\text{RO})_y\text{Si}(\text{CH}_2)_m-\text{R}'$

$\text{R}'' = \text{alkyl}$        $x+y = 2$

5                           $x = 1, 2$

$y = 1, 2$

$\text{R}' = \text{alkyl, aryl}$  (e.g.  $-\text{C}_6\text{H}_5$ )

$-\text{C}_4\text{F}_9$ ,  $-\text{OCF}_2-\text{CHF}-\text{CF}_3$ ,  $-\text{C}_6\text{F}_{13}$ ,  $-\text{O}-\text{CF}_2-\text{CHF}_2$

$-\text{NH}_2$ ,  $-\text{N}_3$ ,  $-\text{SCN}$ ,  $-\text{CH}=\text{CH}_2$ ,

10                         $-\text{OOC}(\text{CH}_3)\text{C} = \text{CH}_2$

$-\text{OCH}_2-\text{CH}(\text{O})\text{CH}_2$

$-\text{NH}-\text{CO}-\text{N}-\text{CO}- (\text{CH}_2)_5$

$-\text{NH}-\text{COO}-\text{CH}_3$ ,  $-\text{NH}-\text{COO}-\text{CH}_2-\text{CH}_3$ ,  $-\text{NH}- (\text{CH}_2)_3\text{Si}(\text{OR})_3$

$-\text{S}_x-(\text{CH}_2)_3\text{Si}(\text{OR})_3$

15 The silane Si 108  $[(\text{CH}_3\text{O})_3-\text{Si}-\text{C}_8\text{H}_{17}]$  trimethoxyoctylsilane can preferably be employed as the silanizing agent.

The following substances can be employed in particular as silazanes:

Silazanes of the type  $\text{R}'\text{R}_2\text{Si}-\text{N}-\text{SiR}_2\text{R}'$

20                        |  
                            H

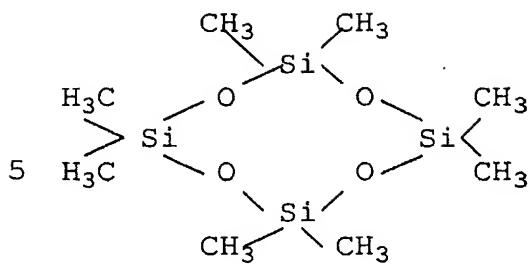
$\text{R} = \text{alkyl}$

$\text{R}' = \text{alkyl, vinyl}$

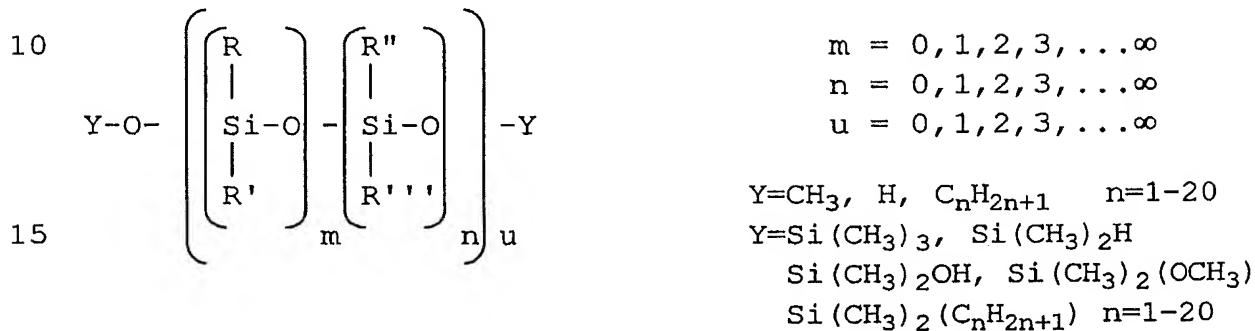
and, for example, hexamethyldisilazane.

25 The following substances can be employed in particular as siloxanes:

Cyclic polysiloxanes of the type D 3, D 4, D 5  
e.g. octamethylcyclotetrasiloxane = D 4



Polysiloxanes or silicone oils of the type



R = alkyl, aryl,  $(CH_2)_n - NH_2$ , H

R' = alkyl, aryl,  $(CH_2)_n - NH_2$ , H

20      R'' = alkyl, aryl,  $(CH_2)_n - NH_2$ , H

R''' = alkyl, aryl,  $(CH_2)_n - NH_2$ , H

The pore structure of the granules according to the invention has predominantly meso- and macropores. The content of pores smaller than 5 nm is not more than 5%, based on the total pore volume.

The granules can comprise as secondary constituents the auxiliary substances, residues of the auxiliary substances which have remained after the heat treatment and/or silane components. The carbon content of the granules according to 30 the invention can be 0 to 15 wt.%.

The particle size distribution of the granules according to the invention can be of a form such that they have a volume content of at least 80% of particles larger than 5  $\mu m$  and at least 80% of particles smaller than 120  $\mu m$ .

35      The invention also provides a process for the preparation of granules based on pyrogenically prepared silicon

dioxide, which is characterized in that pyrogenically prepared silicon dioxide, preferably silicon dioxide prepared from silicon tetrachloride by means of flame hydrolysis, is dispersed in a liquid with an organic or 5 inorganic auxiliary substance, it being possible for the components of the dispersion to be added in any desired sequence, the dispersion is spray dried, the granules obtained are optionally heat-treated at a temperature of 150 to 1,100°C, the granules are optionally silanized and 10 the granules are optionally subjected to a sifting or sieving, it being possible for the last three process steps mentioned to be carried out in any desired sequence.

The dispersion can have a concentration of silicon dioxide of 5 to 40 wt.%. The dispersing can be carried out 15 continuously or discontinuously.

Water, ethanol, propanol, isopropanol, butanol, isobutanol, ethyl acetate or a mixture of these substances can be employed e.g. as the dispersing medium. Water is preferably employed as the dispersing medium.

20 Suitable auxiliary substances for the spray drying are, inter alia, organic auxiliary substances, such as polymers, e.g. cellulose derivatives, polyethylene glycol, waxes, polyolefins, polyacrylates or polyvinyl alcohols, or organic acids, e.g. lactic or citric acid, or inorganic 25 auxiliary substances, such as water-glass, silica sols, aluminium oxide sols or sols of other oxides or tetraethyl orthosilicate. These auxiliary substances can be employed individually or in combination and have the effect of a more uniform shape of the spray particle and a reduced 30 number of particles which have tucks or closed off inner hollow spaces.

In addition, further auxiliary substances which have the effect of lowering the viscosity, and therefore allow a higher degree of filling of the suspension, can optionally

be added. Substances which are suitable for this are, for example, acids, such as formic acid, acetic acid, oxalic acid, hydrochloric acid or nitric acid, bases, such as ammonia, amines or alkali metal, alkylammonium or alkaline earth metal hydroxides, or other substances which have the effect of modifying the surface charge on the dispersed particles.

The auxiliary substances are preferably employed in a low dosage of 0.01 to 10 wt.%, based on the solids content of the dispersion, in order to minimize contamination.

The spray drying can preferably be carried out at an intake temperature of the drying gas of 180 to 700°C and an exit temperature of 50 to 250°C. Disc atomizers or nozzle atomizers can be employed here. Any desired gases can be employed as the drying medium, preferably air or nitrogen.

The optional heat treatment of the granules can be carried out either in a static bed, such as, for example, in chamber ovens, or in an agitated bed, such as, for example, rotary tubular ovens or fluidized bed dryers or calciners.

The optional silanization can be carried out with the same halogenosilanes, alkoxy silanes, silazanes and/or siloxanes as described above, it being possible for the silanizing agent optionally to be dissolved in an organic solvent, such as, for example, ethanol.

The silane Si 108 [(CH<sub>3</sub>O)<sub>3</sub>-Si-C<sub>8</sub>H<sub>17</sub>] trimethoxyoctylsilane can preferably be employed as the silanizing agent.

The silanization can be carried out by a procedure in which the granules are sprayed with the silanizing agent at room temperature and the mixture is then heat-treated at a temperature of 105 to 400°C over a period of 1 to 6 h.

An alternative method of the silanization of the granules can be carried out by a procedure in which the granules are

treated with the silanizing agent in vapour form and the mixture is then heat-treated at a temperature of 50 to 800°C over a period of 0.5 to 6 h.

The heat treatment can optionally be carried out under an 5 inert gas, such as, for example, nitrogen.

The silanization can be carried out continuously or batchwise in heatable mixers and dryers with spray devices. Suitable devices can be, for example: plough share mixers or plate, fluidized bed or flow-bed dryers.

- 10 A wind sifter is preferably employed in the optional sifting, in order preferably to separate off fine particles. Alternatively or in addition, sieving can be employed to separate off coarse particles. The sifting can be carried out at any desired point of the process after 15 the spray drying. Particle fractions which have been separated off can optionally be recycled by admixing them to the starting suspension.

By varying the starting substances, the conditions during spraying, the heat treatment and the silanization, the 20 physico-chemical parameters of the granules, such as the specific surface area, the particle size distribution, the pore volume, the tamped density and the silanol group concentration, pore distribution and pH, can be modified within the stated limits.

- 25 The granules according to the invention can be employed as a support for catalysts, in particular as a support for catalysts for olefin polymerization, the preparation of phthalic anhydride, the preparation of vinyl acetate, the preparation of aniline or the Fischer-Tropsch synthesis.
- 30 They advantageously have a high purity, a high heat stability, a content of micropores of < 5 nm in the total pore volume of less than 5% and a numerical content of particles with tucks or inner hollow spaces in the particle

size range above the D10 value of the particle size distribution weighted according to volume of less than 35%.

The invention also provides the use of the granules as a catalyst support.

### Examples

Silicon dioxides with the following physico-chemical characteristic data are employed as pyrogenically prepared silicon dioxides:

5 Table 1

	AEROSIL 90	AEROSIL 130	AEROSIL 150	AEROSIL 200	AEROSIL 300	AEROSIL 380	AEROSIL OX50
CAS reg. number	112945-52-5 (former no.: 7631-86-9)						
Behaviour towards water	hydrophilic						
Appearance	loose white powder						
BET surface area <sup>1)</sup> m <sup>2</sup> /g	90 ± 15	130 ± 25	150 ± 15	200 ± 25	300 ± 30	380 ± 30	50 ± 15
Average primary particle size nm	20	16	14	12	7	7	40
Tamped density <sup>2)</sup> normal goods g/l compacted goods g/l (added "V")	approx. 80 -	approx. 50 approx. 120	approx. 50 approx. 120	approx. 50 approx. 120	approx. 50 approx. 120	approx. 50 approx. 120	approx. 130 -
Loss on drying <sup>3)</sup> (2 h at 105 °C) % on leaving supply works	< 1.0	< 1.5	< 0.5 <sup>9)</sup>	< 1.5	< 1.5	< 1.5	< 1.5
Ignition loss <sup>4)</sup> (2 h at 1,000°C) %	< 1	< 1	< 1	< 1	< 2	< 2.5	< 1
pH <sup>5)</sup> (in 4% aqueous dispersion)	3.6 - 4.5	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3
SiO <sub>2</sub> <sup>6)</sup> %	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8
Al <sub>2</sub> O <sub>3</sub> <sup>6)</sup> %	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.08
Fe <sub>2</sub> O <sub>3</sub> <sup>6)</sup> %	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.01
TiO <sub>2</sub> <sup>6)</sup> %	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
HCl <sup>8)11)</sup> %	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025
Sieve residue <sup>6)</sup> (acc. to Mocker, 45 µm) %	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.2

- 1) in accordance with DIN 66131
- 2) in accordance with DIN ISO 787/XI, JIS K 5101/18 (not sieved)
- 3) in accordance with DIN ISO 787/II, ASTM D 280, JIS K 5101/21
- 4) in accordance with DIN 55921, ASTM D 1208, JIS K 5101/23
- 5) 5) in accordance with DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24
- 6) in accordance with DIN ISO 787/XVIII, JIS K 5101/20
- 7) based on the substance dried for 2 hours at 105 °C
- 8) based on the substance ignited for 2 hours at 1.000°C
- 9) special packaging protecting against moisture
- 10) 10) in water: ethanol 1 : 1
- 11) HCl content in constituent of the ignition loss

To prepare the silicon dioxides, a volatile silicon compound is injected into an oxyhydrogen gas flame of hydrogen and air. Silicon tetrachloride is used in most cases. This substance hydrolyses to silicon dioxide and hydrochloric acid under the influence of the water formed during the oxyhydrogen gas reaction. After leaving the flame the silicon dioxide enters into a so-called coagulation zone, in which the Aerosil primary particles and primary aggregates agglomerate. The product present as a type of aerosol in this stage is separated from the gaseous concomitant substances in cyclones and then after-treated with damp hot air.

The residual hydrochloric acid content can be lowered to below 0.025% by this process. Since the silicon dioxide is obtained with a bulk density of only approx. 15 g/l at the end of this process, vacuum compaction follows, with which tamped densities of approx. 50 g/l and more can be established.

- 30 The particle sizes of the silicon dioxides can be varied with the aid of the reaction conditions, such as, for example, flame temperature, hydrogen or oxygen content, amount of silicon tetrachloride, residence time in the flame or length of the coagulation zone.
- 35 The BET surface area is determined with nitrogen in accordance with DIN 66 131.

The pore volume is determined via the Hg forcing-in method. For this, the sample is dried for 15 h at 100°C in a drying cabinet and degassed at room temperature in vacuo.

5 The micropores are determined by plotting an N isotherm and evaluating this by the method of BET, de Boer and Barret, Joyner, Halenda. For this the sample is dried for 15 h at 100°C in a drying cabinet and degassed for 1 h at 200°C in vacuo.

10 The particle size distribution is determined by means of the Cilas Granulameter 715 laser-optical particle size analyzer.

The tamped density is determined in accordance with ASTM D 4164-88.

15 The content of particles which have tucks is determined by counting on an SEM photograph of suitable magnification. An uncertainty of an estimated +/- 10% arises due to particles in which the tuck is covered. Section images can be prepared to detect inner hollow spaces. An opening in the particle, the size of which makes up 5-90% of the particle 20 diameter and which opens wider inwards at least a minimal amount is to be evaluated as a tuck. To rule out a numerical over-representation of very fine particles, only some of the particles of which the diameter is above the D10 value of the particle size distribution weighted 25 according to volume are taken into account.

Preparation of the granules according to the invention in example 18

30 The pyrogenically prepared silicon dioxide is dispersed in completely demineralized water, the particular auxiliary substance being admixed. A dispersing unit which operates by the rotor/stator principle is used here. The suspensions formed are spray dried. The finished product is separated off via a filter or cyclone.

The heat treatment of the spray granules is carried out in muffle ovens.

The spray-dried and optionally heat-treated and/or sifted granules are initially introduced into a mixer for the 5 silanization, and are sprayed optionally first with water and then with the silane Si 108 (trimethoxyoctylsilane) or HMDS (hexamethyldisilazane) with intensive mixing. When the spraying has ended, after-mixing is carried out for a further 15 to 30 min, and then heat treatment for 1 to 4 h 10 at 100 to 400°C.

The water employed can be acidified with an acid, for example hydrochloric acid, down to a pH of 7 to 1. The silanizing agent employed can be dissolved in a solvent, such as, for example, ethanol.

15 Detailed information on the preparation and the properties of individual granule examples are to be found in table 2. For comparison, granules were prepared in accordance with 16 US 5776240.

As the SEM photographs of fig. 1-3 demonstrate 20 impressively, the content of particles with tucks is reduced significantly compared with the prior art. Fig. 4 shows that also no noticeable content of inner hollow spaces is present.

Table 2

Example	1	2	3	Comp.	4	5	6	7	8
Starting Aerosil	300	380	380	380	200	300	380	380	380
Spray drying									
Amount of H <sub>2</sub> O (kg)	9.3	9.3	9	9	9.3	9	9	9	9.3
Amount of Aerosil (kg)	0.7	0.7	1	1	0.7	1	1	1	0.7
Auxiliary substance	A	A	B	-	B	C	D	B	A
amount added									
Atomization with	5.6 g	5.6 g	1.5 g	-	5.6 g	5.0 g	10 g	1.5 g	5.6 g
Separation	Disc	Disc	Disc	Disc	Disc	Disc	Disc	Disc	Disc
Heat treatment (h/ <sup>o</sup> C)	-	-	-	-	3/970	-	-	-	3/480
Modification of the surface									
Reagent	-	-	-	-	-	-	-	-	Si 108
Amount [g/100 g Aerosil]	-	-	-	-	-	-	-	-	25
Amount of water [g/100 g Aerosil]	-	-	-	-	-	-	-	-	-
Heating time (h)	-	-	-	-	-	-	-	2	2
Temperature (°C)	-	-	-	-	-	-	-	120	120
Sifting	-	WS/Si	WS/Si	WS/Si	WS	-	-	WS/Si	WS/Si

Physico-chem. data											
BET surface area (m <sup>2</sup> /g)	263	320	315	321	72	271	n.d.	210	194		
Pore volume (ml/g)	1.81	1.6	1.71	1.78	0.54	1.77	n.d.	1.69	1.55		
Content of micropores (< 5 nm) in the total pore volume	< 5 %	< 5 %	< 5 %	< 5 %	< 5 %	< 5 %	< 5 %	< 5 %	< 5 %	< 5 %	
Particle size	d <sub>50</sub> ( $\mu$ m)	36	50	50	56	40	33	31	48	48	
	d <sub>10</sub> ( $\mu$ m)	10	23	18	26				21	20	
	d <sub>90</sub> ( $\mu$ m)	66	77	76	85				74	76	
Tamped density	(g/l)	325	330	320	312				370	390	
Content of particles with tucks (in the size range > D10)						810	n.d.	n.d.			
	< 5 %	< 10 %	< 15 %	80 %	< 5 %	< 10 %	25 %	< 10 %	< 10 %	< 10 %	

Explanations: Auxiliary substances:

- A: carboxymethylcellulose, alkali-free
- B: soda water-glass solution, 38.2%, SiO<sub>2</sub>:Na<sub>2</sub>O = 3.33
- C: methylhydroxypropylcellulose
- D: tetraethyl orthosilicate dissolved in ethanol (50 wt. %)

Sifting:

WS: wind sifting

Si: sieving

## Patent claims

1. Granules based on pyrogenically prepared silicon dioxide with the following physico-chemical characteristic data:

Average particle diameter: 10 to 120  $\mu\text{m}$   
BET surface area: 40 to 400  $\text{m}^2/\text{g}$   
Pore volume: 0.5 to 2.5 ml/g  
Pore distribution: content of pores of pore diameter < 5 nm in the total pore volume of less than 5%, remainder meso- and macropores  
Tamped density: 220 to 1,000 g/l  
Numerical content of particles in the particle size range above the D10 value of the particle size distribution weighted according to volume which have tucks or closed off inner hollow spaces: < 35 %

2. Process for the preparation of granules according to claim 1, characterized in that pyrogenically prepared silicon dioxide is dispersed in a liquid, preferably water, with one or more auxiliary substances, it being possible for the components of the dispersion to be added in any desired sequence, the dispersion is spray dried, the granules obtained are optionally heat-

dried at a temperature of 150 to 1,100°C, the granules are optionally silanized and/or the granules are optionally subjected to a sifting or sieving, it being possible for the particle size fractions separated off optionally to be recycled. The optional process steps of heat treatment, silanization and sieving or sifting can be carried out in any desired sequence.

3. Process according to claim 2, characterized in that one or more components from the following substances are used as auxiliary substances: polymers, e.g. cellulose derivatives, polyethylene glycol, waxes, polyolefins, polyvinyl alcohols or polyacrylates, acids, e.g.

formic, acetic, lactic, oxalic, nitric, hydrochloric or citric acid, bases, e.g. ammonia, amines or alkali metal, alkylammonium or alkaline earth metal hydroxides, sols, e.g. silica sols, aluminium oxide sols or sols of other oxides, water-glass or silicic acid esters, e.g. tetraethyl orthosilicate.

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4. Process according to claim 2, characterized in that one or more components from the following substances are used as auxiliary substances: carboxymethylcelluloses, 10 methylcelluloses or celluloses etherified with other alcohols, water-glass or silica sol.

**INTERNATIONAL SEARCH REPORT**

International Application No  
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A. CLASSIFICATION OF SUBJECT MATTER	IPC 7 C09C1/30	C01B33/18	B01J2/04	B01J35/10	B01J21/08
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According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09C B01J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 198536 Derwent Publications Ltd., London, GB; Class A25, AN 1985-222307 XP002227356 & SU 1 139 701 A (PHYS CHEM IND TESTI), 15 February 1985 (1985-02-15) abstract	2,3
Y	---	4
A	---	1
Y	WO 96 34062 A (GRACE GMBH ;BELLIGOI PETER (DE); FIELD REX (DE); LUEERS GEORG (DE)) 31 October 1996 (1996-10-31) claims 1-7,9 page 3, line 16 -page 5, line 11 examples 1,3	4
A	---	1-3
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

15 January 2003

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/10857

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 398 021 A (STAMICARBON B. V.) 16 February 1979 (1979-02-16) claims 1-3,6-9 page 5, line 1 - line 16 page 6, line 35 -page 7, line 9 examples 2,4	2,3
A	---	1
X	EP 0 442 325 A (GRACE GMBH) 21 August 1991 (1991-08-21) page 3, line 35 - line 47	2,3
A	---	1
A	DATABASE WPI Section Ch, Week 198336 Derwent Publications Ltd., London, GB; Class A60, AN 1983-756843 XP002227357 & SU 963 950 A (AS UKR PHYS CHEM), 4 February 1983 (1983-02-04) abstract	1-3
A	---	
A	EP 0 725 037 A (DEGUSSA) 7 August 1996 (1996-08-07) the whole document & US 5 776 240 A 7 July 1998 (1998-07-07) cited in the application	1,2
A	---	
A	EP 0 598 318 A (DEGUSSA) 25 May 1994 (1994-05-25) example 4	1-4
A	---	
A	DATABASE CA 'Online' CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SAITO, SHIGERU: "Silica gel catalysts for the manufacture of adiponitrile" retrieved from STN Database accession no. 78:4774 CA XP002227355 abstract & JP 47 023284 B (MITSUBISHI RAYON CO., LTD.) 29 June 1972 (1972-06-29)	
A	---	
A	DATABASE WPI Section Ch, Week 199330 Derwent Publications Ltd., London, GB; Class E36, AN 1993-239797 XP002227358 & JP 05 163013 A (NIPPON STEEL CHEM CO), 29 June 1993 (1993-06-29) abstract	
	-----	

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/EP 02/10857

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
SU 1139701	A	15-02-1985	SU	1139701 A1		15-02-1985
W0 9634062	A	31-10-1996	DE AT AU BR CA DE DE WO EP JP US	19516253 A1 181945 T 5760296 A 9608182 A 2219120 A1 69603179 D1 69603179 T2 9634062 A1 0822965 A1 11504354 T 6103004 A		31-10-1996 15-07-1999 18-11-1996 04-05-1999 31-10-1996 12-08-1999 09-03-2000 31-10-1996 11-02-1998 20-04-1999 15-08-2000
FR 2398021	A	16-02-1979	NL AT AT BE CA DE ES FR GB IT JP JP NL SE US US	7707961 A .373853 B 494178 A 868792 A2 1126244 A1 2831561 A1 471789 A1 2398021 A1 2001044 A , B 1107453 B 1406663 C 54021992 A 62015485 B 7807220 A 7807949 A 4228260 A 4225464 A		22-01-1979 27-02-1984 15-07-1983 08-01-1979 22-06-1982 01-02-1979 01-10-1979 16-02-1979 24-01-1979 25-11-1985 27-10-1987 19-02-1979 08-04-1987 22-01-1979 21-03-1979 14-10-1980 30-09-1980
EP 0442325	A	21-08-1991	DE DE AT AU AU BR CA CS DE DE EP FI NO PL US ZA MX	4004468 C1 4032619 A1 119929 T 638544 B2 7093691 A 9100472 A 2035675 A1 9100382 A2 69108071 D1 69108071 T2 0442325 A1 910696 A 910580 A 289063 A1 5221337 A 9100565 A 9100499 A1		22-08-1991 16-04-1992 15-04-1995 01-07-1993 15-08-1991 29-10-1991 15-08-1991 15-09-1991 20-04-1995 20-07-1995 21-08-1991 15-08-1991 15-08-1991 23-09-1991 22-06-1993 27-11-1991 05-06-1992
SU 963950	A	07-10-1982	SU	963950 A1		07-10-1982
EP 0725037	A	07-08-1996	DE CA CN DE EP ES	19601415 A1 2168677 A1 1134399 A , B 59606530 D1 0725037 A1 2154748 T3		08-08-1996 05-08-1996 30-10-1996 12-04-2001 07-08-1996 16-04-2001

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/EP 02/10857

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
EP 0725037	A		JP 3095989 B2 JP 8253309 A KR 190472 B1 PT 725037 T SG 42921 A1 US 5776240 A	10-10-2000 01-10-1996 01-06-1999 31-07-2001 17-10-1997 07-07-1998
EP 0598318	A	25-05-1994	DE 4336548 A1 AT 182484 T AT 190346 T DE 4345168 A1 DE 5930970 D1 DE 59309970 D1 DK 598318 T3 EP 0598318 A1 EP 0807669 A2 ES 2136109 T3 JP 6296851 A US 5480626 A	19-05-1994 15-08-1999 15-03-2000 03-11-1994 02-09-1999 13-04-2000 29-11-1999 25-05-1994 19-11-1997 16-11-1999 25-10-1994 02-01-1996
JP 47023284	B		NONE	
JP 5163013	A	29-06-1993	JP 3170016 B2	28-05-2001